Journal of the Arkansas Academy of Science

Volume 67 Article 37

2013

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# Molecular Structure of Pentahaptocyclopentadienebis(tetrahydrothiophene)triphenylphosphineruthenium(II) triflate

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Running Title: Molecular Structure of $[CpRu(PPh_3)(tht)_2]Otf$

The synthesis of $[CpRu(PPh_3)(tht)_2]Otf$ (tht = tetrahydrothiophene; Otf = triflate), **I**, was previously reported by Nave and coworkers (Nave et al. 1999). Compound **I** is a useful starting material, because it reacts with excess thietane (thie) (Nave et al. 2001) or pentamethylene sulfide (pms) (Nave et al. 1999) to give the di-thie or di-pms complexes, respectively. Herein, we report on the molecular structure of **I**.

Single crystals of **I** were obtained by the slow diffusion of hexane into a $CH_2Cl_2$ solution of **I**. The crystallographic data are given in Table 1. A yellow crystal (0.10 x 0.14 x 0.28 mm) was mounted on a glass fiber with silicone rubber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Cell constants were obtained from a least-squares refinement using the setting angles of 24 reflections in the range $17.0 < 2\theta < 22.0^o$. The intensities of three standard reflections measured after every 60 min. of X-ray exposure time showed a drift of 1.3 %. A total of 6171 reflections (5843 unique reflections, $R_{int} = 0.02$) were collected using the θ-2θ scan technique to a maximum 2θ value of $50^o$. The data were corrected for Lorentz and polarization effects and a psi-scans absorption correction was applied. Neutral atom scattering factors were taken from Cromer and Waber (1974). Anomalous dispersion effects were included in $F_{calc}$, the values of Δf' and Δf'' were those of Cromer (Cromer 1974).

The structure was solved by direct methods and refined by full matrix least-squares. The final cycle of the full matrix least-squares refinement was based on 3154 observe reflections ($I > 3.00\ \sigma(I)$) and 386 parameters and converged with $R = 0.045$, $R_w = 0.060$. The β-carbons on one of the tht ligands was disordered. These atoms (C29, C30) were refined isotropically with a 50% occupancy factor. The thermal ellipsoid of C28 suggests it may also be slightly disordered, but the disorder was not enough to support splitting of that atom into two components. All hydrogen atoms were constrained to idealized positions (C-H = 0.95 A, U = Uc + 0.01). Selected bond distances and angles are given in Table 2.

Table 1. Crystal, data collection and refinement parameters for $[CpRu(PPh_3)(tht)_2]Otf$.

| | |
|---|---|
| Formula | $RuS_3P\ F_3O_3C_{32}H_{36}$ |
| Formula weight | 753.85 |
| Temperature (K) | 293 |
| Unit cell dimensions | |
| a (Å) | 10.675(2) |
| b (Å) | 11.089(2) |
| c (Å) | 14.858(3) |
| α ($^o$) | 70.898(18) |
| β ($^o$) | 88.050(17) |
| γ ($^o$) | 88.869(17) |
| V (Å$^3$) | 1660.9(6) |
| $D_{calc}$ (g/cm$^3$) | 1.51 |
| Space group | triclinic $P_1$- |
| Z | 2 |
| F(000) | 770.3 |
| λ (Å) | 0.7107 |
| μ (mm$^{-1}$) | 0.74 |
| 2θ range ($^o$) | 4 to 50 |
| Absorption correction | analytical |
| Total reflections | 6171 |
| Unique reflections | 5843 |
| R for merge | 0.020 |
| Data for refinement | 3154 |
| Parameters | 386 |
| R(F), Rw(F) | 0.045, 0.060 |
| GOF | 0.90 |
| Largest diff. peak and hole | 0.42(9), -0.42(9) |

The structure of **I** is seen in Figure 1. The Ru atom is coordinated to a π-bound cyclopentadienyl ligand,

the phosphorus atom of the triphenylphosphine and two S-bound tht ligands. Selected bond distances and angles are given in Table 2.

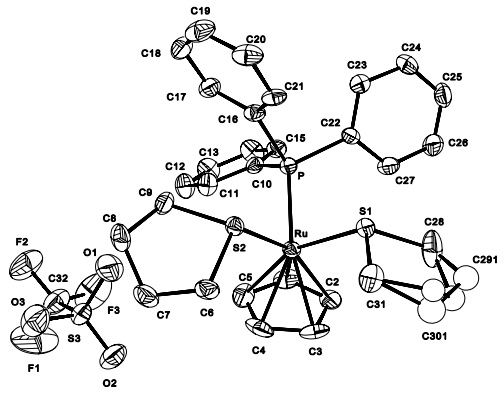


Fig. 1. Ortep of **I** showing atom labeling scheme. Hydrogens have been omitted for clarity.

Table 2. Selected bond distances (Å) and angles (°) for **I**.

| | | | |
|---|---|---|---|
| Ru-S1 | 2.370(2) | S1-Ru-S2 | 82.45(8) |
| Ru-S2 | 2.379(2) | S1-Ru-P | 91.65(8) |
| Ru-P | 2.318(2) | S2-Ru-P | 91.30(7) |
| S1-C28 | 1.818(11) | Ru-S1-C28 | 114.0(4) |
| S1-C31 | 1.838(10) | Ru-S1-C31 | 110.8(3) |
| S2-C6 | 1.838(8) | C28-S1-C31 | 92.1(5) |
| S2-C9 | 1.834(9) | Ru-S2-C6 | 111.8(3) |
| C6-C7 | 1.509(13) | Ru-S2-C9 | 114.5(3) |
| C7-C8 | 1.504(14) | C6-S2-C9 | 93.7(4) |
| C8-C9 | 1.517(12) | S2-C6-C7 | 105.1(6) |
| C28-C291 | 1.39(3) | C6-C7-C8 | 106.7(7) |
| C28-C292 | 1.52(3) | C7-C8-C9 | 106.5(7) |
| C291-C301 | 1.41(3) | S2-C9-C8 | 105.6(6) |
| C292-C302 | 1.57(3) | S1-C28-C291 | 111.4(11) |
| C301-C31 | 1.59(3) | S1-C28-C292 | 105.3(11) |
| C302-C31 | 1.43(2) | C28-C291-C301 | 110.4(19) |
| | | C28-C292-C302 | 107.5(16) |
| | | C291-C301-C31 | 112.5(18) |
| | | C292-C302-C31 | 101.4(15) |
| | | S1-C31-C301 | 103.9(10) |
| | | S1-C31-C302 | 108.2(9) |

The Ru-S bond distances of 2.370(2) and 2.379(2) Å are slightly shorter than the Ru-S bond distance of 2.395(2) Å in the mono-tht complex $[CpRu(PPh_3)_2(tht)]BF_4$ (Jiang et al. 1996). The slighter shorter distances in **I** may be due to the loss of one of the bulky $PPh_3$ ligands upon coordination of the second tht. A significant decrease in the Ru-P distance is seen in **I** as compared to the Ru-P distances in the mono-tht compound (2.318(2) Å compared to 2.366(2) and 2.367(2) Å).

## Supplemental Materials

Supplemental materials (atomic coordinates, bond distances and angles) are available from the authors upon request.

## Acknowledgments

The authors thank Arkansas State University and the Department of Chemistry and Physics for their support of this project.

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